

## REMOVAL OF EXCESS FLUORIDE FROM WATER BY ALUMINUM HYDROXIDE

Beneberu Shimelis, Feleke Zewge\* and Bhagwan Singh Chandravanshi

Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia

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**ABSTRACT.** The efficiency of untreated hydrated alumina (UHA) and thermally treated hydrated alumina (THA) obtained from hydrolysis of locally manufactured aluminum sulfate to remove fluoride from aqueous solution has been investigated in batch and continuous operation. The parameters considered were contact time and adsorbent dose, thermal pre-treatment of adsorbent, initial fluoride concentration and pH. The adsorption was rapid during the initial 20 min, but significant amount (> 90 %) was removed within one hour at an optimum adsorbent dose of 1.6 g/L for initial F<sup>-</sup> concentration of 20 mg/L. The removal efficiency of F<sup>-</sup> was increased with adsorbent dosage. Fluoride adsorption efficiencies increase with increase in the thermal treatment temperature up to 200 °C, but further increase in temperature resulted in decreased removal efficiency. For application in continuous packed bed column, treatment at 300 °C was taken as an optimum value. Fluoride adsorption capacity increases linearly with increase in F<sup>-</sup> concentration. High defluoridation efficiency was achieved using both UHA and THA within a pH range of 4.0 to 9.0. The adsorption data at ambient pH were well fitted to the Freundlich isotherm model with a minimum capacity of 23.7 mg F<sup>-</sup>/g and 7.0 mg F<sup>-</sup>/g for THA and UHA, respectively. The kinetic studies showed that the adsorption reaction of fluoride removal by hydrated alumina can be well described by a pseudo-second-order rate equation. Continuous packed bed column experiment using THA indicated that 4.5 g of THA could treat 6 L of water containing 20 mg/L fluoride before breakthrough. Hence, both UHA and THA can be applied for the treatment of water with high fluoride content.

**KEY WORDS:** Fluoride, Defluoridation, Hydrated alumina, Fluoride removal efficiency, Adsorption capacity, Adsorption kinetics, Breakthrough

## INTRODUCTION

Fluoride has certain physiological properties [1, 2] of great interest in relation with the human health and wellbeing. The role of fluoride in the normal process of mineralization of certain (hard) tissues is highly evident [3, 4]. Albeit the beneficial effects, it has much detrimental effects when its presence exceeds the threshold limit [5]. Mottling of teeth is one of the earliest and most easily recognized symptoms of dental fluorosis [6]. In severe fluorosis some victims can experience deformation of bones (skeletal fluorosis) and eventually becomes crippling. Prevalence of dental and skeletal fluorosis has been reported in several parts of the world including Ethiopia, where fluoride concentration in drinking water exceeded the guideline level [7]. The WHO guidelines published in 1996 has set a maximum amount of fluoride in drinking water as 1.5 mg/L to protect human from fluorosis [8]. However, up to 33 ppm of F<sup>-</sup> concentrations were reported in water samples from boreholes in Ethiopia. Such high levels are found in the Rift Valley Region, which is characterized by a relatively high volcanic activity in the country [9-12]. Consequently, problems related to intake of high fluoride water are prevalent in this region of the country [9, 11].

Possible control options to protect fluorosis may include provision of alternative source of water, blending with low fluoride containing water, provision of bottled water, at least for young persons, treatment of water supply at sources and at the point of use. In an area where alternative sources are not easily available and the provision of bottled water is not economical, as in the case of the Rift Valley Regions of Ethiopia, treatment of contaminated water is the most reasonable approach.

Several attempts have been made to reduce the fluoride to an acceptable level in drinking water over the years, using a wide variety of materials. The Nalgonda technique, where alum is

\*Corresponding author. E-mail: zewge@chem.aau.edu.et

mixed with lime, has been introduced in many countries, e.g. India, Kenya, Senegal, Ethiopia, and Tanzania [13, 14]. Reverse osmosis [15], aluminum electrodes and electro-dialysis [16], fly ash [17], ion-exchange resins [18], clay [19], aluminum and calcium salts [20, 21] have been tested and/or applied. Defluoridation of water by activated alumina is the method of choice in developed countries [15]. Adsorption of fluoride onto activated alumina has been practiced even in developing countries like India [22]. It has been widely used for removal of F<sup>-</sup> from drinking water and is one of the most popular materials used in the defluoridation of waters [23-27].

In Ethiopia there are few treatment options that have been studied for removing excessive levels of fluoride in water. Low cost methods such as adsorption on clays [14, 28] and other locally available materials like diatomaceous earth [29] and bone [14] have been considered in few studies. It is important to note that the applicability of these low cost methods is limited due to inefficiency. Recent studies in Ethiopia indicated the possibility of using locally produced aluminum sulfate and lime combination [14]. Based on results of intensive investigation at the Department of Chemistry of Addis Ababa University in collaboration with the Catholic Relief Service (CRS), community scale defluoridation unit has been tested at pilot scale and implemented in three villages [14]. However, this technique is associated with limitations such as the requirement of high chemical dose on daily basis, large sludge volume, sludge disposal problem, inefficiency with water sources having high total dissolved solid and complexity of operation under rural setting [10]. Furthermore, results of laboratory investigations and operational experiences at community scale indicated that the application of this process for water containing fluoride concentration exceeding 10 mg/L is not feasible from economic and water quality points of view [14]. A method based on adsorption on laboratory-produced alumina made by thermal decomposition of locally produced aluminum sulfate was also tested [29]. However, this method requires higher temperature (900-950 °C). Furthermore, adsorption by imported activated alumina has been practiced in Wonji-Shoa and Methara Sugar Estates since 1962, but all the plants are not functional at present [14, 28], which is attributed to the higher running costs. Hence, there is a need for the development of alternative technologies that take into account of local conditions from technical and economic points of view.

Thus, the objective of this study was to develop efficient household and community scales water defluoridation techniques based on locally produced aluminum sulfate. The present studies were carried out on synthetic fluoride solutions with the objective of establishing process parameters.

## EXPERIMENTAL

*Defluoridation material preparation.* The adsorbent (aluminum hydroxide, also called hydrated alumina) was prepared from Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.14H<sub>2</sub>O (17 % Al<sub>2</sub>O<sub>3</sub>). The raw material, which was purchased from Awash Melkasa Aluminum Sulfate and Sulfuric Acid Factory (Awash Melkasa, Ethiopia), was dissolved in distilled water and the pH was adjusted to 7 with 2 M NaOH. The pH was chosen based on the literature value at which hydrated alumina [Al(OH)<sub>3</sub>] become stable [29]. The precipitate (hydrated alumina) was filtered, washed with distilled water and dried, hereafter considered as untreated hydrated alumina (UHA). Samples of the UHA were placed in porcelain crucibles and heated at the preset temperature from 200 to 600 °C at 100 °C intervals in a furnace (Carbolite, ELF Model) for 1 h. The heating times were selected based on preliminary screening tests. At the end of 1 h, the treated samples were taken out from the furnace and kept in a desiccator until further use. This material hereafter was considered as treated hydrated alumina (THA).

*Reagents and standard solutions.* A 1000 mg F/L sodium fluoride stock solution (99.0 % NaF, BDH Chemicals Ltd Poole, England) was prepared in distilled water. Standards and F<sup>-</sup> spiked

samples at a required concentration range were prepared by appropriate dilution of the stock solution with distilled water. The total ionic strength adjustment buffer (TISAB) was prepared following a recommended procedure, except that EDTA replaced CDTA [30].

*Instrumentation.* A pH/ISE meter (Orion Model, EA 940 Expandable Ion Analyzer, U.S.A.) equipped with combination fluoride-selective electrode (Orion Model 96-09) was employed for the determination of F<sup>-</sup>. The pH was measured with pH/ion meter (WTW Inolab pH/ION Level 2, Germany) using unfilled pH glass electrode. The residual F<sup>-</sup> concentration was measured according to the procedure described in the instrument's manual by using 1:1 ratio of the samples or standards and TISAB. The electrode was calibrated prior to each experiment over a concentration range of interest. All measurements were made at room temperature ( $23 \pm 2$  °C).

*Batch adsorption experiments.* All batch experiments were conducted using 500 mL of distilled water spiked with F<sup>-</sup> in 1 L Erlenmeyer flask under continuous mixing condition with magnetic stirrers at room temperature ( $23 \pm 2$  °C). A sample (a supernatant solution) was periodically (as required) taken out from the flask and filtered through a 0.2 µm filter paper (ADVANTEC) before fluoride analysis. The percent adsorption efficiency and the defluoridation capacity at a given contact time for the selected adsorbents were determined [10].

The effect of adsorbent dose and contact time were studied by varying the dosages of untreated adsorbent from 0.4 to 2.0 g/L at constant initial F<sup>-</sup> concentration of 20 mg/L. This value was selected based on the range of fluoride concentration in waters of the Rift Valley of Ethiopia. To investigate the effect of thermal treatment on fluoride removal efficiency of THA, 1.6 g/L dose of each adsorbent treated at different temperatures (200 to 600 °C) was mixed with 20 mg/L fluoride solution for a contact time of 1 h. The effects of initial F<sup>-</sup> concentration and contact time were investigated by varying the fluoride concentrations from 5 to 30 mg/L at constant THA dose of 1.6 g/L. The effect of pH of raw (F<sup>-</sup> spiked) water on the adsorption of F<sup>-</sup> onto both UHA and THA was studied by varying the initial pH of the water from 3 to 10. The pH was adjusted to the desired level either with 0.1 M NaOH or 0.1 M HCl. Data for plotting the adsorption isotherm were obtained by mixing a constant F<sup>-</sup> concentration of 50 mg/L with 9 series of increasing dosages of both adsorbents in the range from 0.4 to 2.0 g/L. The adsorbent-liquid mixture was agitated for a contact time of 24 h to ensure equilibrium. The kinetic analysis of the adsorption data is based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms. It was determined using a F<sup>-</sup> surface loading of 31.25 mg F<sup>-</sup>/g of both treated and untreated adsorbents (1.6, 0.8 and 0.4 g/L adsorbents for the corresponding F<sup>-</sup> concentrations of 50.0, 25.0 and 12.5 mg F<sup>-</sup>/L, respectively). The change in pH during adsorption of F<sup>-</sup> on THA was determined by first equilibrating constant adsorbent dose of 1.6 g in 490 mL distilled water samples whose pH varies from 3 to 10 for 20 h. Then, 10 mL of a 1000 mg/L F<sup>-</sup> stock solution was added so that the initial F<sup>-</sup> concentration was 20 mg/L. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH. The pH was measured at different times after addition of 10 mg/L F<sup>-</sup>.

*Continuous column experiments.* Continuous flow defluoridation study was carried out using a column made from glass with internal diameter and effective bed height of 0.9 cm and 25 cm, respectively. The column was packed with 4.5 g of THA sample with particle size range of 1.0 - 2.8 mm. Spiked water containing 20 mg/L F<sup>-</sup> was introduced into the column at a flow rate of 4 mL/min with peristaltic pump (Gilson Minipuls 3, Sweden) up-flow direction. The influent and effluent concentrations of fluoride were measured at a fixed time interval, to monitor the performance of the column. Breakthrough times were determined and used to calculate breakthrough volumes and adsorption capacities of the columns. The fluoride adsorption capacity was determined when the effluent fluoride concentration at the top of the column beds

exceeded 1.5 mg/L (the permissible concentration, designated as the break-through concentration) and also at the point of saturation.

## RESULTS AND DISCUSSION

*Effect of adsorbent dose and contact time.* The results of the study of the effect of untreated adsorbent dose and contact time on the fluoride removal are presented in Figures 1 and 2 for UHA mass of 0.2, 0.4, 0.6, 0.8 and 1.0 g at constant initial fluoride concentration of 20 mg/L. The results show that under the condition specified above, a contact time of about 60 min is enough to remove about 90 % of the fluoride in solution with an adsorbent dose greater than or equal to 1.6 g/L. This indicates that longer contact time did not have much effect.

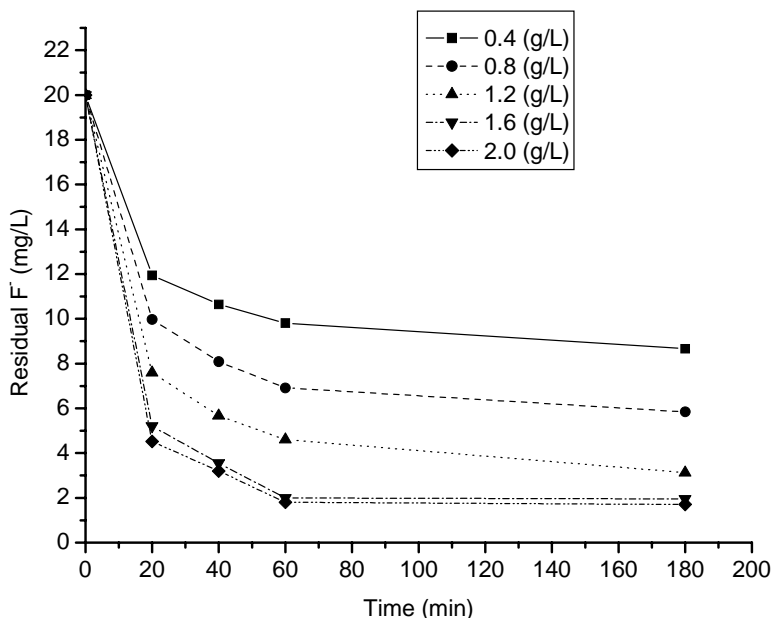


Figure 1. Residual  $F^-$  concentration as a function of time for different doses of UHA (initial concentration = 20 mg/L  $F^-$ , initial pH =  $7.0 \pm 0.3$ ).

The defluoridation efficiency was significantly increased as the dose increases as reflected by the measured residual fluoride concentration (Figure 2). The percent removal of  $F^-$  increased significantly up to adsorbent dose of 1.6 g/L, but no significant change was observed beyond this dose under the experimental condition used. The increase in  $F^-$  adsorption is possibly due to the increase availability of  $F^-$  binding sites resulting from an increase in adsorbent dosage.

On the other hand, the adsorption capacity decreases with increasing dose (Figure 2). This is possibly due to the fixed initial fluoride concentration. To maintain reasonable capacity and high removal efficiency, the surface loading (i.e., the mass ratio of fluoride to adsorbent dose) should be lower than the optimum value. The surface loading for optimum fluoride removal (about 90 %) obtained from Figure 2 is 12.5 mg/g or less. A dose of 1.6 g/L corresponding to the capacity of about 11.25 mg  $F^-$ /g of adsorbent was considered for further adsorption experiments.

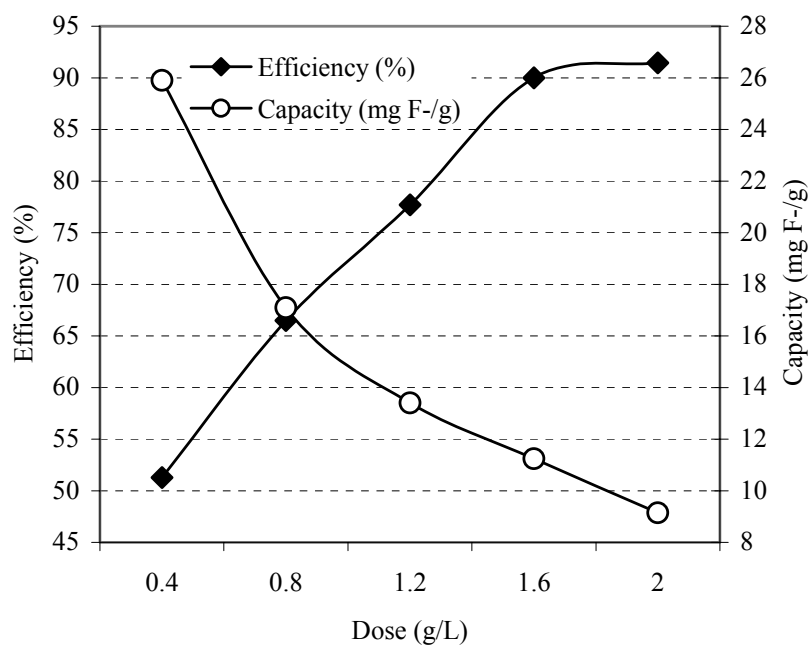


Figure 2. Capacity and efficiency (%) of  $F^-$  removal as a function of UHA dose (initial concentration = 20 mg/L  $F^-$ , contact time = 60 min, initial pH =  $7.0 \pm 0.3$ ).

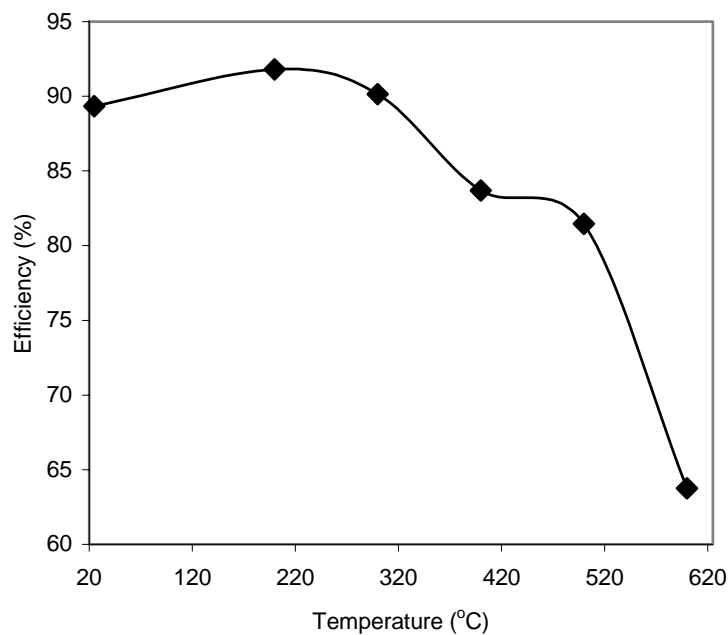


Figure 3. Effect of thermal treatment on  $F^-$  removal efficiency of the adsorbent (dose = 1.6 g/L, initial concentration = 20 mg/L  $F^-$ , contact time = 60 min, initial pH =  $7.0 \pm 0.3$ ).

*Effect of thermal treatment.* Figure 3 shows change in the fluoride removal efficiency as a function of adsorbent thermal treatment temperatures. As can be seen, fluoride adsorption efficiencies increase with increase in the thermal treatment temperature up to 200 °C, but further increase in temperature resulted in decreased removal efficiency. It was reported that when aluminum hydroxide is heated at lower temperatures, a series of alumina are formed. At about 200 °C, alumina loses its water content and gets hardened [31]. It is reported that this transitional alumina produced at low temperatures converts to alpha-alumina (corundum), which is the most stable crystalline form of alumina, at higher temperature (1200-1300 °C). It is probably due to the resulting loss of constitutional OH<sup>-</sup> that causes decrease in removal efficiency. The relatively increasing F<sup>-</sup> removal up to 200 °C may be due to the increased removal of physically adsorbed and/or constitutional water molecules. Although the fluoride removal efficiency was high for the adsorbent treated at 200 °C (Figure 3), the material strength may not be good enough (preliminary laboratory investigation shows the material gets powdered during preparation for column packing) for application in continuous packed bed column. Therefore, the adsorbent treated at 300 °C with significant removal efficiency (> 90 %) was used in further studies.

*Effect of initial concentration and contact time.* The set of data reported for the effect of the F<sup>-</sup> concentrations was obtained by varying the initial fluoride concentrations at constant THA dose of 1.6 g/L. As clearly shown in Figure 4 and Figure 5, the efficiency increases with decreasing initial F<sup>-</sup> concentration at the initial stage of adsorption.

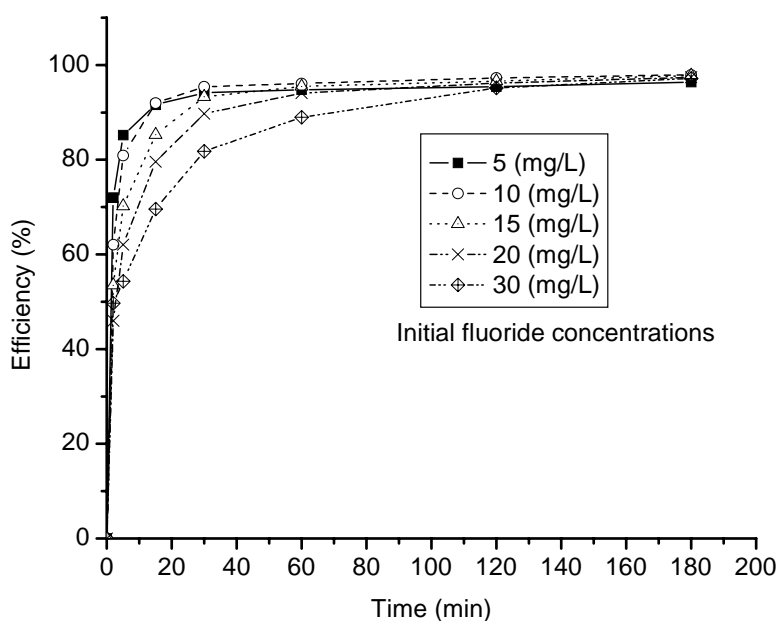


Figure 4. Fluoride removal efficiency as a function of contact time (adsorbent dose = 1.6 g/L, 300 °C treated adsorbent, initial pH = 7.0 ± 0.3).

As can be seen from Figure 5, the initial F<sup>-</sup> concentration had an influence on F<sup>-</sup> sorption time. Significant fluoride removal efficiency (> 90 %) was observed when the initial fluoride was less than or equal to 20 mg/L for a contact time of 60 min. For a lower initial fluoride concentration (e.g. 10 mg/L) significant amount of F<sup>-</sup> was removed within 15 min. This indicates

that sufficient contact time is required for higher initial fluoride concentration, to achieve effective removal.

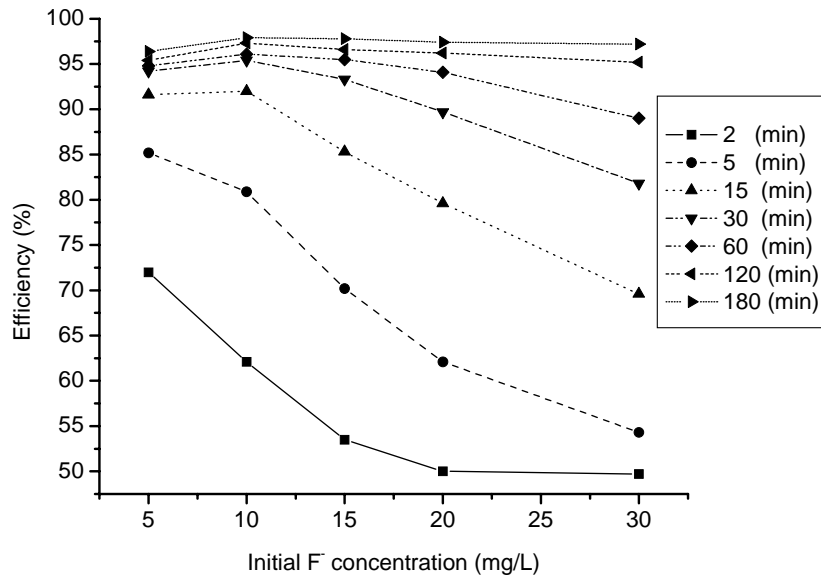


Figure 5. The variation of fluoride removal efficiency as a function of initial fluoride concentration at different contact times (adsorbent dose = 1.6 g/L, 300 °C treated adsorbent, initial pH = 7.0 ± 0.3).

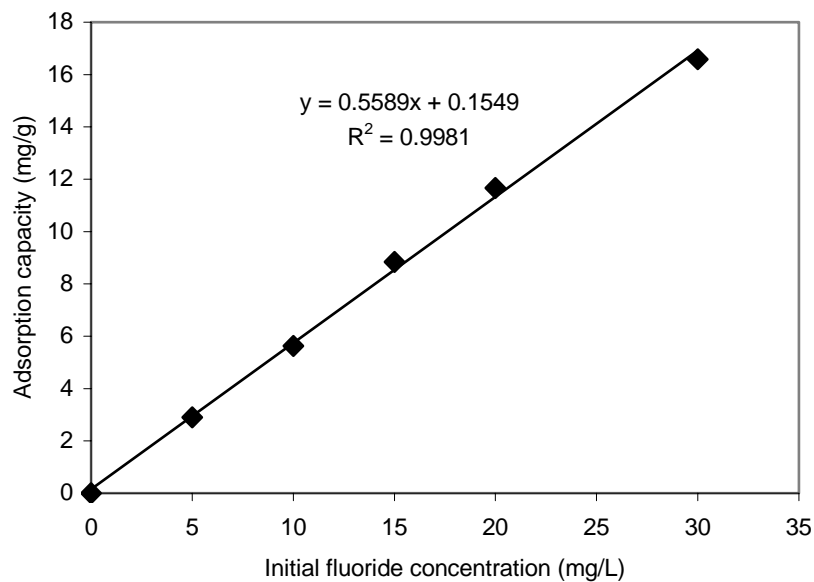


Figure 6. Effect of initial fluoride concentration on the adsorption capacity of thermally treated adsorbent (treatment temperature = 300 °C, adsorbent dose = 1.6 g/L, contact time = 60 min, initial pH = 7.0 ± 0.3).

On the other hand, for a given mass of adsorbent, the fluoride removal capacity increases with increasing initial concentration (Figure 6). This can be attributed to the utilization of less accessible or energetically less active sites because of increased diffusivity and activity of fluoride upon the increased concentration [4]. The adsorption sites present on the interior surface of a pore may not be as easily accessible because of the resistance to the pore diffusion. This result indicates that it is possible to estimate capacity for the different initial fluoride content of the water.

*Adsorption isotherm.* Figure 7 shows an adsorption isotherm, which is the relationship between the bulk aqueous phase activity (concentration) of adsorbate and the amount adsorbed at constant temperature. In this study, the general purpose Langmuir (not shown) and Freundlich adsorption isotherm models were used. The isotherm experiments were carried out at 9 different dosages of both untreated and treated adsorbents in a range from 0.4 to 2.0 g/L. As can be seen from the figure, the fluoride removal capacity of both adsorbent increases and never reached at point of saturation. The equilibrium adsorption capacity of the treated adsorbent, however, was higher than the untreated adsorbent.

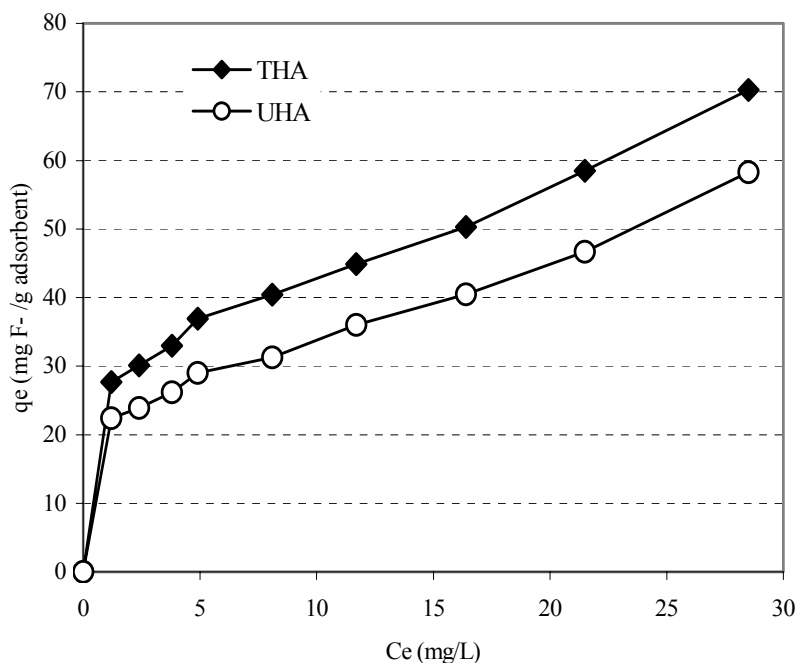


Figure 7. Adsorption isotherm of different doses of UHA and THA (initial  $F^-$  concentration = 50 mg/L, contact time = 24 h, initial pH =  $7.0 \pm 0.3$ ).



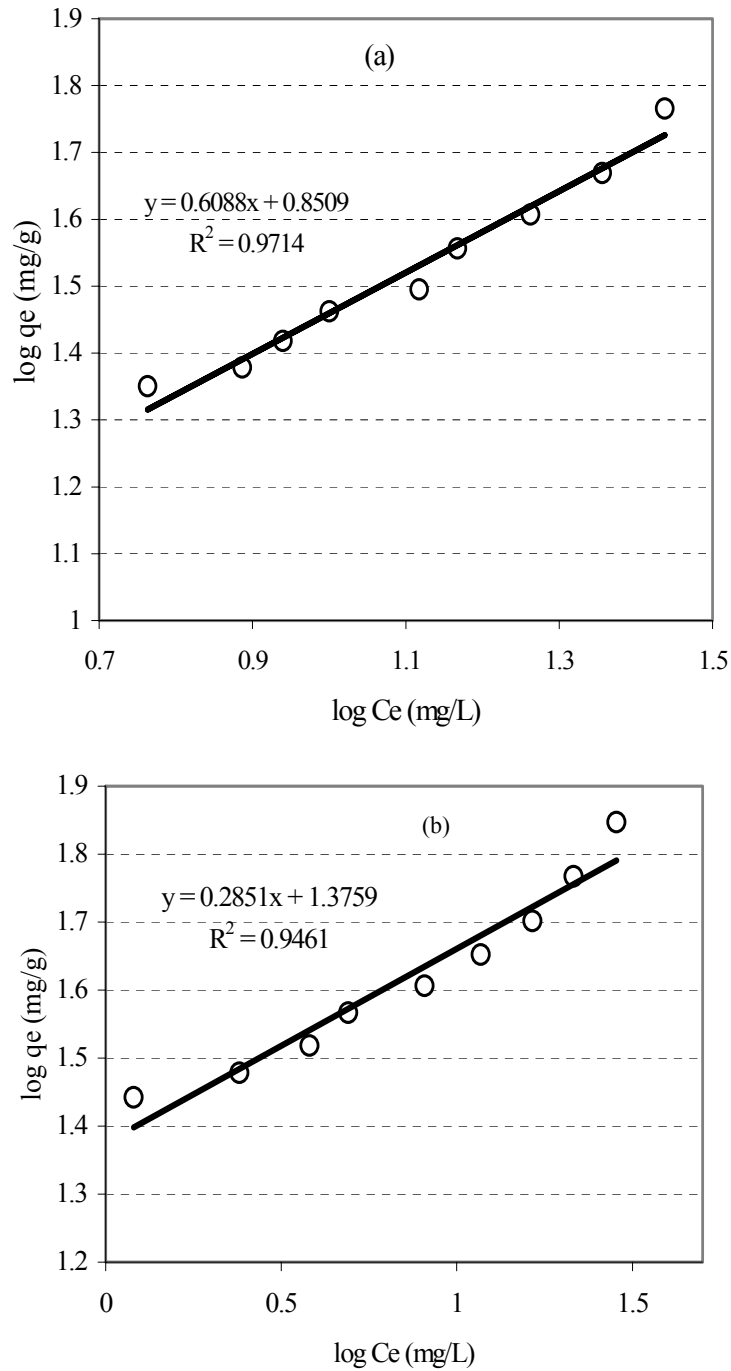


Figure 8. Linear Freundlich isotherm of THA (a) and UHA (b) (initial concentration = 50 mg/L F<sup>-</sup>, equilibrium contact time = 24 h, ambient pH = 7.0 ± 0.3).

The Freundlich equation is presented below in both the standard form and linearized form, respectively [30].

$$q_e = K_F C_e^{1/n} \quad (1)$$

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad (2)$$

where  $q_e$  is the amount of fluoride adsorbed per unit weight of adsorbent (mg/g) at equilibrium,  $C_e$  is the equilibrium fluoride concentration (mg/L),  $K_F$  is the measurement of the adsorption capacity (mg/g) based on Freundlich isotherm, and  $1/n$  is the adsorption intensity.

The Freundlich parameters along with correlation coefficients were obtained for both adsorbents. The minimum adsorption capacities can be determined by plotting  $\log(q_e)$  vs.  $\log(C_e)$  (Figure 8a, b). The results indicate that the experimental fluoride adsorption data well fitted to Freundlich isotherm, and the correlation coefficient was above 0.97 with the minimum adsorption capacity of about 7.0 mg/g for UHA and about 23.7 mg/g for THA (Table 1). But the data did not fit well to the Langmuir isotherm model (not shown). This is possibly due to the heterogeneous nature of the surface of the adsorbent.

Table 1. Freundlich parameters for the adsorption isotherm (initial concentration = 20 mg/L F<sup>-</sup>, adsorbent dose = 1.6 g/L, contact time = 60 min).

| Material | $K_F$ (mg/g) | Equation                              | $1/n$  | $R^2$  |
|----------|--------------|---------------------------------------|--------|--------|
| UHA      | 7.0404       | $\log q_e = 0.6117 \log C_e + 0.8476$ | 0.6117 | 0.9730 |
| THA      | 23.7192      | $\log q_e = 0.2875 \log C_e + 1.3751$ | 0.2875 | 0.9450 |

*Adsorption kinetics of fluoride.* The fluoride adsorption kinetics of both adsorbents have been studied for initial fluoride concentrations of 50.0, 25.0 and 12.5 mg/L with the corresponding adsorbent dose of 1.6, 0.8, 0.4 g/L, respectively, for each adsorbent. The residual fluoride concentrations as a function of time are shown in Figure 9 (a, b).

As can be seen from Figure 9, initially the rate of adsorption of fluoride onto adsorbents (UHA and THA) was very fast especially for UHA. The changes in the rate of removal may be due to the fact that, initially, all adsorbents sites were vacant and the fluoride concentration gradient was high. Afterwards the fluoride uptake rate by the adsorbents decreased significantly due to decreased adsorption sites.

The kinetic analysis of the adsorption of fluoride on both adsorbents was studied based on reaction kinetics of pseudo-second-order mechanisms by using the Lagergren rate equation as shown below [33]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \text{or} \quad \frac{d(q_e - q_t)}{(q_e - q_t)^2} = -k_2 dt \quad (3)$$

The integrated form at boundary conditions ( $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ ) gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (4)$$

where  $q_e$  and  $q_t$  are amount of adsorbed fluoride at equilibrium and any time  $t$  (mg/g solid material) respectively,  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is equilibrium rate constant of second-order sorption, and  $t$  is the reaction time (min).  $k_2$  can be determined by plotting  $t/q_t$  against  $t$  based on Eq. (4). The larger the  $k_2$  value, the slower the adsorption rate.

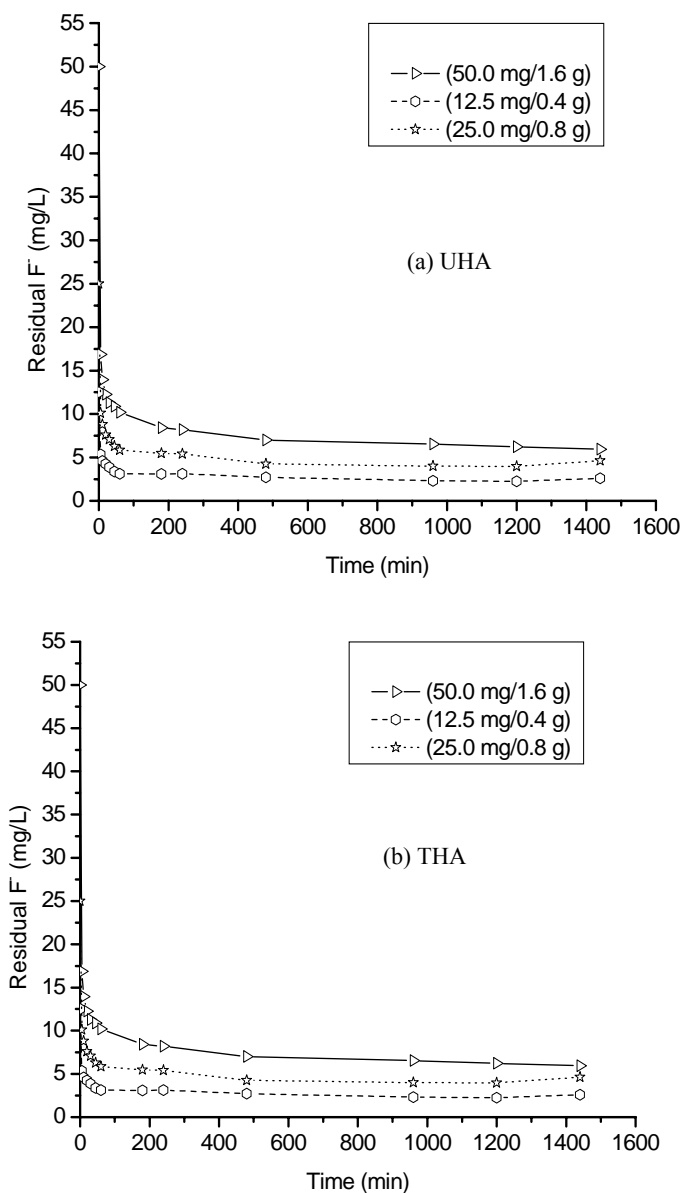


Figure 9. Adsorption kinetics of fluoride on UHA (a) and THA (b) adsorbents each with initial F<sup>-</sup> concentrations to adsorbent dose of 50.0, 25.0 and 12.5 mg/L, and 1.6, 0.8 and 0.4 g/L, respectively (ambient pH = 7.0 ± 0.3, contact time = 24 h, particle size = 0.1 mm).

It was shown earlier that the treated adsorbent exhibit the highest fluoride adsorption capacity compared to the untreated one. However, the equilibration time was relatively longer in the case of treated adsorbent (Figure 9). This longer time is possibly due to the decrease in surface area resulting during heat treatment. Further investigation is required to clarify this point. Figure 10 (a, b) shows the pseudo-second-order plot of fluoride adsorption kinetics on both UHA and THA at three different initial fluoride concentrations for each adsorbent with the

same surface loading. Since the rate constants for the three initial fluoride concentration of each adsorbent were close to each other, it can be averaged to get a single rate constant as shown in Figure 11. The values of rate constants obtained under different initial concentrations are summarized in Table 2.

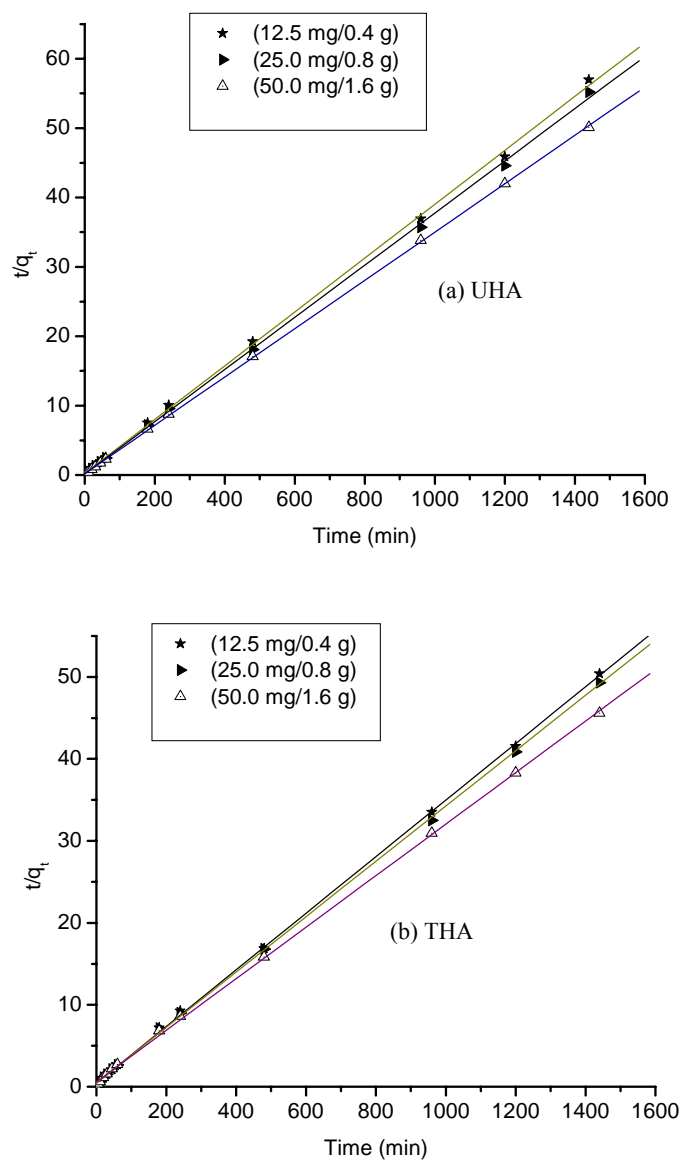


Figure 10. Lagergren plot for the removal of fluoride at different initial concentrations on both UHA (a) and THA (b) adsorbents (ambient pH = 7.0 ± 0.3, particle size ≤ 1 mm).

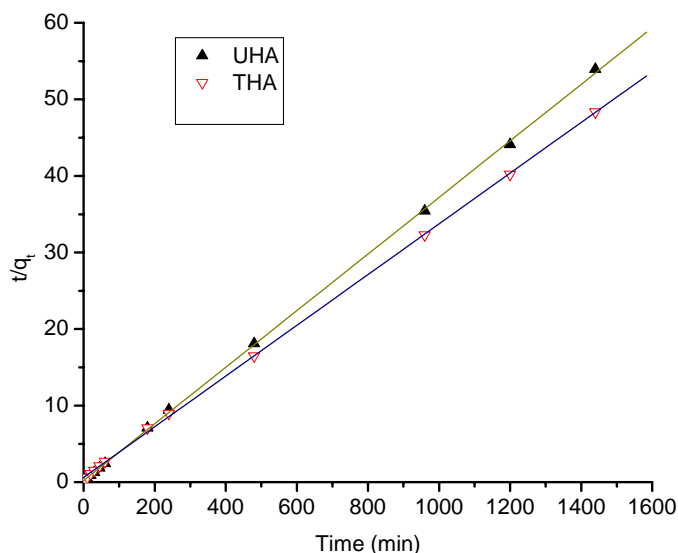


Figure 11. Lagergren plot for the removal of fluoride (average values of three different initial concentration) for both UHA and THA adsorbents at constant surface loading of 31.25 mg/g (ambient pH = 7.0 ± 0.3, particle size = <1 mm).

Table 2. Pseudo-second-order rate constants (adsorbent dose = 1.6 g/L, contact time = 60 min).

| Material | Initial conc. g/L) | $k_2$ (g min <sup>-1</sup> mg <sup>-1</sup> ) (x 10 <sup>-3</sup> ) | Rate equation              | R <sup>2</sup> |
|----------|--------------------|---|----------------------------|----------------|
| UHA      | 12.5               | 6.13  | $t/q_e = 0.0388t + 0.2456$ | 0.9997         |
|          | 25.0               | 8.52  | $t/q_e = 0.0376t + 0.1659$ | 0.9998         |
|          | 50.0               | 5.75  | $t/q_e = 0.0348t + 0.2106$ | 0.9999         |
|          | Average            | 6.80 ± 1.50   |                            | 0.9998         |
| THA      | 12.5               | 2.34  | $t/q_e = 0.0345t + 0.5087$ | 0.9999         |
|          | 25.0               | 2.05  | $t/q_e = 0.0337t + 0.5534$ | 0.9999         |
|          | 50.0               | 1.44  | $t/q_e = 0.0314t + 0.6870$ | 0.9998         |
|          | Average            | 1.94 ± 0.46   |                            | 0.9999         |

*Effect of raw water pH.* Figure 12 shows the influence of initial solution pH on the fluoride removal efficiency of both treated and untreated adsorbents. Both UHA and THA exhibit maximum uptake at raw (simulated) water pH of 4, but no significant difference was observed in the pH range 4 to 9. The decrease in the fluoride removal below pH 4.0 is possibly due to increasing protonation of the fluoride ions in the aqueous phase ( $pK_a$  of HF = 3.17), whereas at pH greater than 9.0 is considered to be due to competition from hydroxide ions at the adsorption sites, since both OH<sup>-</sup> and F<sup>-</sup> have the same charge and similar ionic radii [4]. This is in agreement with the work done by Liyh, *et al.* [5] who also found, a broad pH range of significant adsorption for activated alumina. In the same paper [23], it was reported that activated alumina of the type Alcoa F1 exhibit maximum uptake at pH 5.0. The decrease in removal as pH is raised from 5 to 8 was around 12 % with type G-87 and 40 % with Alcoa F1, where as it is 3.3 % and 1.3 % with THA and UHA, respectively, in this study. So, application of defluoridation technology with both THA and UHA generally do not require any pre-treatment or post-treatment to adjust the pH. In addition, other studies have shown that the

soluble aluminofluoro complexes are formed at  $\text{pH} < 6$  resulting in the presence of aluminum ion in the treated water [32]. Hence, they suggest that it may be preferable to carry out defluoridation at  $\text{pH} > 6$ .

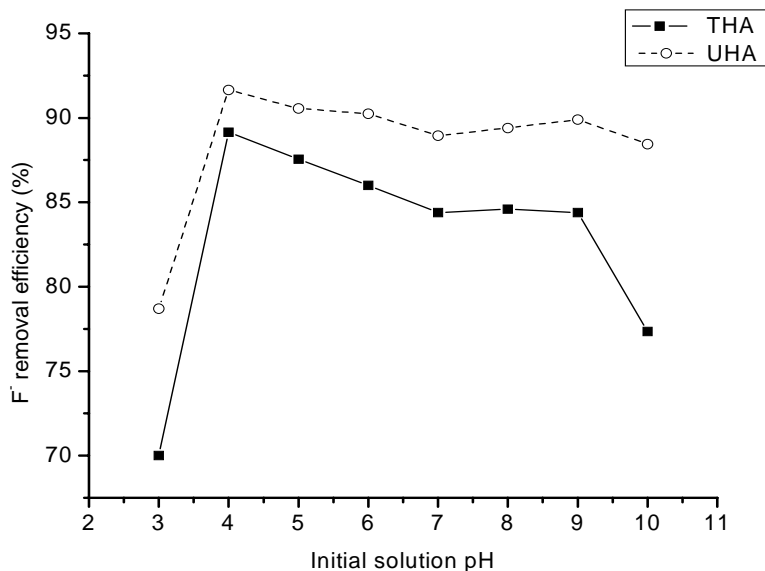
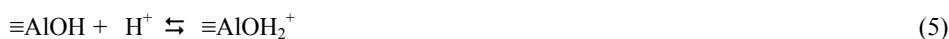


Figure 12. Effect of initial water pH on fluoride removal efficiency of both THA and UHA (initial concentration = 20 mg/L  $\text{F}^-$ , adsorbent dose = 1.6 g/L, contact time = 60 min).

*Change in pH during adsorption.* The extent of adsorption of anions is strongly governed by the pH of the solution. It is considered that anion adsorption is coupled with a release of  $\text{OH}^-$  ions. The adsorption of fluoride on UHA and THA is considered as a two step ligand exchange reaction:



Which, combined, gives



where  $\equiv\text{AlOH}$  represents the solid surface.

The pH of the aqueous solution is an important variable which controls the adsorption process. Hence, the change in pH during the adsorption process was studied after the addition of  $\text{F}^-$  solutions to properly equilibrate THA suspensions.  $\Delta\text{pH}$  was calculated by taking the difference between initial and final pH. The initial,  $\text{pH}_i$ , is the pH after 20 h equilibration of the substrate at a particular pH level.

A plot of  $\Delta\text{pH}$  vs. the initial pH value for THA shown in Figure 13 reveals important characteristics of the adsorption process. In the pH range 4.5 to 6, a slight rise in  $\Delta\text{pH}$  was observed after addition of  $\text{F}^-$  to the test sample of treated adsorbent in the acid form. The rise in pH is particularly strong at short time intervals. The result reveals that the change in pH is

maximum at pH 6.0. This is in agreement with fluoride removal studies on activated alumina by other workers [34]. At a pH above 6,  $\Delta\text{pH}$  decreases sharply as a result of stronger competition from hydroxide ion.  $\Delta\text{pH}$  is also found less in acidic range; this may be as a result of the formation of weakly ionized hydrofluoric acid. It can be noted that, after addition of  $\text{F}^-$  all  $\Delta\text{pH}$  values are positive, indicating an increase in pH after addition of fluoride.

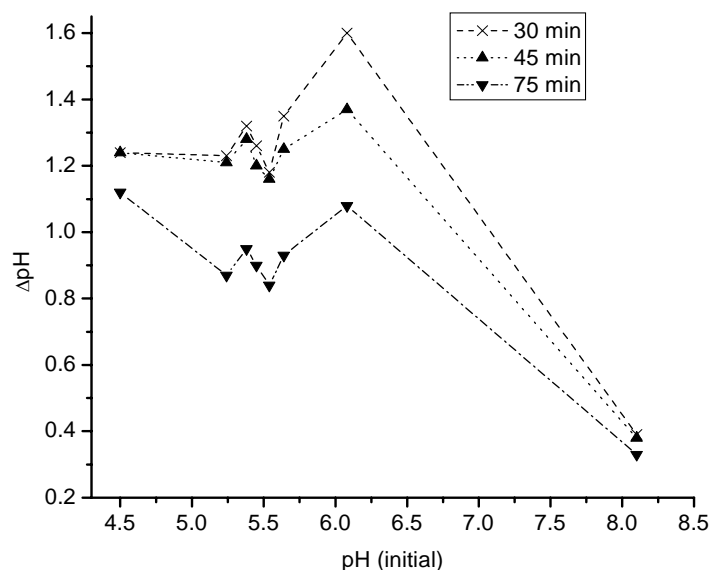


Figure 13.  $\Delta\text{pH}$  vs the initial pH for THA at different times after the addition of 20 mg/L  $\text{F}^-$  solution (dose = 1.6 g/L, conc. 20 mg/L  $\text{F}^-$ , alumina treated at 300 °C).

*Performance of the packed column.* Figure 14 shows the breakthrough of fluoride in a column fed with aqueous solution of  $\text{F}^-$ . The influent concentration of fluoride to the column was 20 mg/L. As shown in Figure 14, the fraction of fluoride remaining in the effluent of the column was maintained at values less than 0.075 (or 1.5 mg/L) until 400 bed volume of water is treated. This corresponds to about 6 L of water containing 20 mg/L  $\text{F}^-$ . This indicates that, about 4.5 kg of THA is enough to produce about 6000 L of  $\text{F}^-$  safe water ( $\text{F}^- < 1.5$  mg/L) that is sufficient for a household consisting of four family members each consuming 4 L of water per day for more than a year. The sorption capacity of THA was estimated to be 23.2 mg/g at breakthrough (1.5 mg/L) and 38.7 mg/g at point of saturation. The capacity at breakthrough was comparable with the minimum fluoride adsorption capacity of 23.7 mg/g obtained from batch experiment. Further research is underway to optimize the column parameters, to regenerate the exhaust adsorbent and to investigate the effect of other ions by using distilled water spiked with major ions that are commonly existing in groundwater and also using real water samples from the Rift Valley Region.

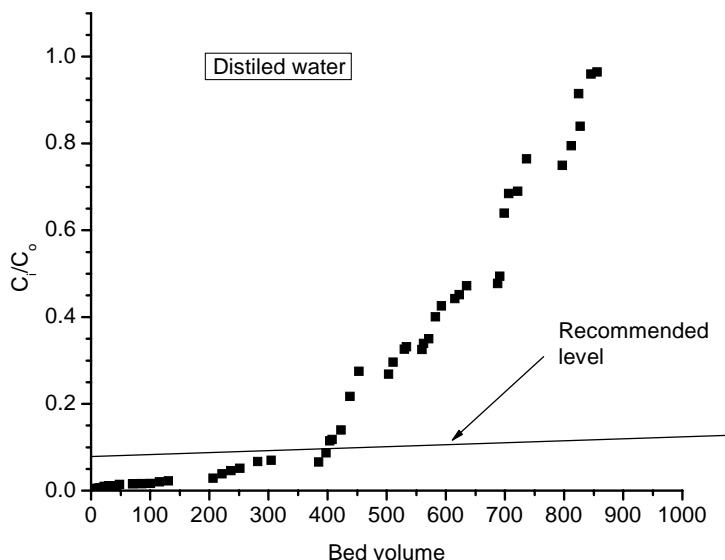


Figure 14. Breakthrough curve for the adsorption of fluoride onto THA ( $C_0 = 20$  mg/L, mass of adsorbent = 4.5 g, flow rate = 4 mL/min, bed height = 25 cm, internal diameter = 0.9 cm).

## CONCLUSIONS

In the present work, a simple, fast, and promising method for the treatment of fluoride contaminated water is developed. Both UHA and THA showed a superior adsorption capacity for fluoride ion. Based on the results obtained, it can be concluded that greater than 90 % of fluoride was removed within 1 h at an optimum adsorbent dose of 1.6 g/L for initial  $F^-$  concentration of 20 mg/L. Fluoride adsorption capacity increases linearly with increase in  $F^-$  concentration. High defluoridation efficiency was achieved using both UHA and THA with in a pH range of 4.0 to 9.0. The adsorption data is well fitted to the Freundlich isotherm model with a minimum capacity of 23.7 mg  $F^-$ /g and 7.0 mg  $F^-$ /g for THA and UHA, respectively. The kinetic studies showed that the adsorption reaction of fluoride removal by hydrated alumina can be well described by a pseudo-second-order rate equation. Moreover, continuous packed bed column experiment using THA indicated that 4.5 g of THA could treat 6 L of water containing 20 mg/L fluoride before break through.

The fluoride removal capacity of UHA and THA used in the present study was about 7 mg  $F^-$ /g and 23 mg  $F^-$ /g of adsorbent, respectively, which are higher than the literature value reported for activated alumina (1.8-1.9 mg  $F^-$ /g) [4]. Furthermore, it was demonstrated that the adsorbent can be applicable in batch as well as in continuous operations to suit defluoridation either at household or small community level. Laboratory results in batch operation indicated that the minimum  $F^-$  removal capacity of THA was 23.7 mg  $F^-$ /g, which means that 6 L of water containing 20 mg  $F^-$ /L (i.e. 120 mg  $F^-$ ) can be treated by about 5 g of THA, which is comparable to the amount required (4.5 g THA) to treat the same amount of water (6 L) with the same  $F^-$  concentration (20 mg/L) in continuous operation.



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